CHAPTER III
ATMOSPHERIC TRANSPORT AND DEPOSITION PROCESSES

Section 112(m) of the Clean Air Act (CAA) directs EPA, in cooperation with the National Oceanic and Atmospheric Administration (NOAA), to assess the extent of atmospheric deposition of hazardous air pollutants to the Great Waters. As part of this assessment, EPA is directed to, among other things, monitor atmospheric deposition of pollutants, investigate pollutant sources and deposition rates, and conduct research to improve monitoring methods. Accomplishing these tasks requires an understanding of the processes by which the pollutants of concern are transported from their emission sources and deposited to the Great Waters. Researchers use mathematical models of atmospheric transport and deposition of pollutants to analyze the movement of pollutants in the environment, to develop relationships between sources and receptors of pollutants, and to evaluate prospective control strategies.

This chapter introduces some basic concepts and scientific terms that are relevant to atmospheric transport and deposition of pollutants, and that are used throughout this report. It also discusses general types of transport and deposition models, focusing on modeling achievements of the most recent years and on efforts by EPA and NOAA plus other researchers, mostly in academia. Further discussion of the uses of a few of these models is included in Chapter IV.

There is currently a general understanding of the major factors that affect the transport of air pollutants between their sources and receptors, as well as how these factors interrelate. The development of new models and refinement of existing ones have been advanced in recent years, as shown in this chapter. Research on the characterization of sources, processes, and parameters has continued in parallel with monitoring efforts. The Great Waters have been and will continue to be the focus of many of the investigations presented in this chapter.

Despite recent advances in our understanding of transport and deposition of contaminants in the atmosphere, there is still a paucity of data with which to calibrate models (measurement of dry deposition and source inventories are typical examples). Further analysis is also required for some transport and deposition phenomena, such as the importance of environmental cycling of contaminants emitted and deposited in the past.

This chapter is divided into three sections. Section III.A discusses some key terms, such as deposition and environmental cycling. Section III.B presents a brief description of general types of transport and deposition models. Section III.C compares some models that have been recently used in Great Waters studies, and discusses modeling and data limitations.

III.A Atmospheric Deposition and Environmental Cycling

Long-range atmospheric transport and deposition of pollutants have been widely acknowledged to make a significant contribution to contaminant inputs to surface waters, including the Great Waters. Atmospheric deposition refers to the removal of pollutants (following transport) from the air to soil, water, and other surfaces. Deposition may occur directly to the water surface and/or indirectly to the land surface in the watershed, with subsequent runoff from rainfall carrying contaminants to the waterbody. It is important to

recognize that both local and distant air emission sources may contribute to the pollutant loading at a given location and time. Also, pollutants may be emitted from a combination of point, mobile, or area sources; or even from resuspension in the air of previously deposited material.

There are three major processes of direct atmospheric deposition to natural waterbodies: wet deposition, dry deposition, and gas exchange across the air-water interface. A schematic of these processes is presented in Figure III-1. In addition to these processes, cycling of semi-volatile compounds (e.g., polychlorinated biphenyls (PCBs)) and persistent compounds among environmental media (e.g., air, water, sediment) can be an important input of pollutants in waterbodies.

FIGURE III-1
Atmospheric Deposition Processes
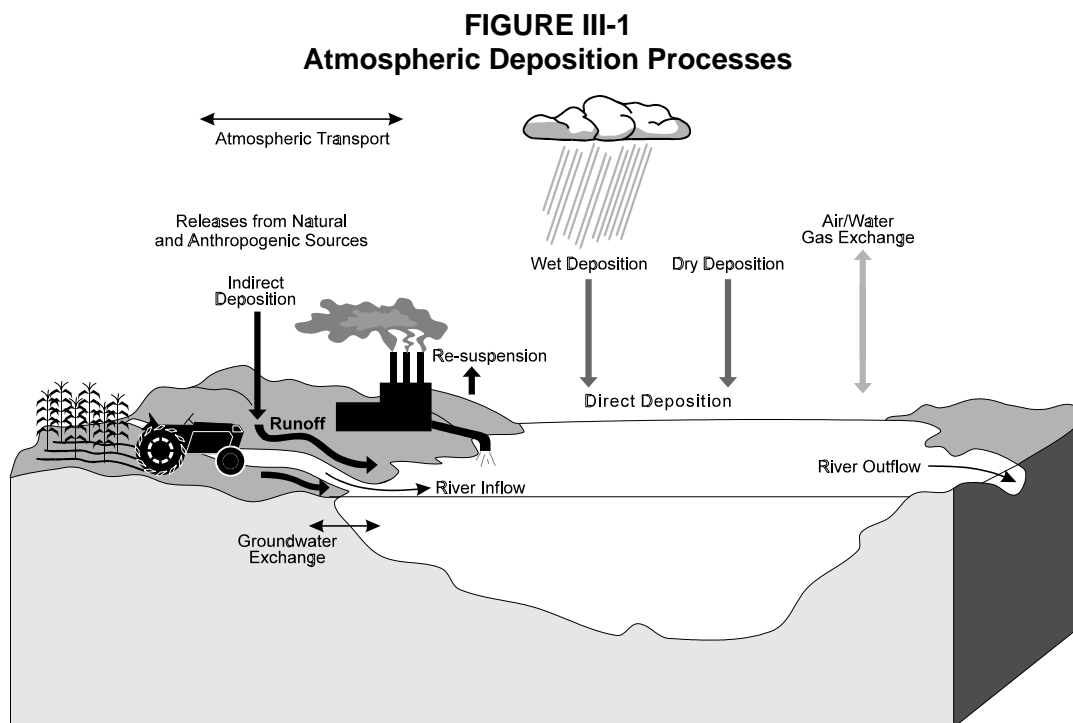
Monitoring and assessment of these processes provide important information on the atmospheric contribution of a given pollutant to a specific site, as well as extent of deposition of the pollutant. Hence, monitoring at Great Waters study sites requires meteorological measurements and measures of contaminant concentrations very near to the site and, if possible, over the surface of the waterbody itself. Understanding of these processes allows researchers to evaluate quantitatively the long-term distribution of a pollutant in an aquatic system. EPA sponsors research on atmospheric deposition so that future monitoring can become less research-oriented and more focused on evaluating trends in atmospheric loading of pollutants and determining the effects resulting from efforts to reduce emissions.

Wet Deposition

Wet deposition (or in more general terms, removal via precipitation) refers to the incorporation of both gases and particles into cloud droplets and into "hydrometeors" (e.g., snow, sleet, and rain) where they are carried to the Earth's surface in precipitation. Pollutants may be removed from air by wet deposition through three main mechanisms:

(1) minute pollutant-bearing particles can serve as cloud condensation nuclei and become naturally embedded into water droplets during cloud formation; (2) particles may be incorporated into falling hydrometeors by collisions; or (3) gaseous pollutants may be dissolved into cloud droplets and falling rain. Cloud and precipitation droplets, therefore, may contain pollutants in both particulate and dissolved forms. The removal of gases by wet deposition is dependent on their solubilities in the elements of precipitation. Wet deposition is essentially an intermittent process, although if precipitation events are frequent or long-lasting, wet deposition may be the major pathway for deposition of air pollutants, specifically for totally particulate species (e.g., metals other than mercury). For semi-volatile compounds, air-water gas exchange appears to be a dominant factor (Hoff et al. 1996).

To get useful and quantitative measurements of wet deposition, well-prepared protocols and quality assurance approaches are designed and used, with careful handling of field equipment, samples, and subsequent chemical analyses. For example, wet deposition rates are determined using collectors that are designed to open only during precipitation events. Work must be designed and carried out so as to minimize measurement problems with the samples that can arise from chemical or biological activity, evaporation of gaseous pollutants, or possible contamination during storage and handling. The concentrations of most of the pollutants of concern in any one precipitation event may be small, so rather advanced field and chemical-analytical methods are needed for quantitatively assessing the concentrations. Though measurements must be taken of short-term events in which the concentrations may be small, it is important to track the concentrations of the pollutants of concern deposited over time because of their persistence and tendency to bioaccumulate. Thus, the kind of monitoring used in the Great Waters program involves research into new and more accurate monitoring techniques and must be carefully designed to focus efforts on well-located sites, protocols, and methods.

Dry Deposition

Dry deposition refers to removal from the air of pollutants (bound to particles or in the gaseous form) to the land or water surface in the absence of precipitation. Dry deposition is essentially a continuous process and often represents a substantial removal of the pollutants from the atmosphere. The pollutants reach the surface by the turbulent movements of the air or, for large particles, through gravitational settling. Dry deposition of particulates with high deposition velocities is an important contribution to pollutant loadings to waterbodies located near

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Research on Dry Deposition

In 1994, a research program was established among the EPA, the University of Michigan, the Illinois Institute of Technology, Carnegie-Mellon University, and Oak Ridge National Laboratory to develop and test new techniques for measuring dry deposition of mercury and other trace elements to natural water surfaces. The data will be used to develop new mathematical models for predicting dry deposition onto water surfaces under a variety of atmospheric and surface conditions. Measurement methodologies have been developed and tested, and modeling is underway. Field studies in 1996-1997 are planned to gather basic data, and to compare with model predictions.

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cities. For large open waterbodies, air-water gas exchange appears to contribute more than dry particle deposition (Hoff et al. 1996). A review of models of dry deposition to water is presented by Zufall and Davidson (1997).

Dry deposition is measured from pollutant accumulation on artificial surfaces (e.g., a plexiglass plate). Alternatively, atmospheric pollutant concentrations and their mass-size distribution can be combined with micrometeorology data to model dry deposition rates. The major difficulty in measuring dry deposition is that there is no method that can be routinely used because the flux density is so low and because the exchange rate is usually governed by details of the surface that cannot be reproduced in artificial devices. The difficulties of measuring dry deposition have motivated new research on measurement methodologies and modeling of dry deposition under the Great Waters program (see sidebar on the previous page).

Gas Exchange Across the Air-Water Interface

In addition to wet and dry deposition of pollutants, gaseous pollutants may be directly exchanged between air and water (i.e., transferred in either direction across the air-water interface). The gaseous exchange of organic compounds at the air-water interface is an important phenomenon in the balance of pollutants occurring in air and water (Eisenreich et al. 1997), and extensive North American waterbodies, such as the Great Lakes and Chesapeake Bay, provide large surface areas for this exchange to occur. Analogous gas exchange phenomena occur between plants and air, and land and air.

Gas exchange is a two-way process involving both *gas absorption* or invasion (air to water) and *volatilization* or evasion (water to air) across an air-water interface of a volatile chemical (usually in gaseous form under every-day conditions) or a semi-volatile chemical (e.g., polycyclic aromatic hydrocarbons (PAHs), PCBs). The direction of gas movement (from air to water or from water to air) depends on the fugacity difference (i.e., the relation of the Henry's law scaled air concentration to the water concentration). The direction of gas exchange will tend to reduce this difference and move toward a near-equilibrium condition. The direction and magnitude of gas transfer is a function of the chemical concentrations in air and water, wind speed, temperatures in air and water, waves (height, frequency), physical and chemical properties of the pollutant (e.g., molecular weight, vapor pressure, Henry's Law constant, solubility), and in some cases characteristics of the water (e.g., pH for acidic and basic species, and salinity in estuaries).

Gas absorption and volatilization occur simultaneously, even when near-equilibrium has been achieved. Taken together, volatilization and gas absorption contribute to the *net flux* (the difference between the amount of pollutant invading and the amount evading) or effective movement of a chemical across the air-water interface. Net flux may be expressed as the mass of gas moving across a unit of area over a unit of time (e.g., 8 ng per m^2 of water surface per day). To achieve quantitative estimates for the Great Waters of net deposition of pollutants of concern, many of which are semi-volatile, such physical and chemical processes must be quantified so they may be correctly used in models. Some earlier work on pollutant loading made simplifying assumptions of "one-way" flux or deposition without quantifying gas exchanges, but recent work shows the need for more complete representation of the natural processes for each pollutant. Furthermore, it is important in some cases to determine both absorption and volatilization, instead of net flux alone. Even under conditions close to air-water equilibrium, with small net flux, the absorption and volatilization may be quite large, making gas exchange a key factor in the analysis of pollutant movements (see Table IV-2 in Section IV.A on the Great Lakes).

There are two models commonly used to describe gas exchange at the air-water interface. The Stagnant Two-film Model (Liss and Slater 1974; Whitman 1923) is used to estimate gas exchange at low wind speeds, which results in an essentially stagnant boundary layer just above the water. However, as higher wind speeds generate more turbulence in the boundary layers of both air and water, turbulent eddies bring small parcels of water to the surface, where they begin to equilibrate with the atmosphere, and more rapid gas exchange of chemicals occurs. To characterize this situation, the Surface Renewal Model may be used, but the choice of model for a given situation is not always clear-cut. The air-water gas exchange models continue to be improved to incorporate new factors such as effect of bubbles, breaking waves, and surface films. For a review of these models, readers should refer to Theofannous (1984) and Eisenreich et al. (1997).

Environmental Cycling of Semi-Volatile Compounds

The exchange and cycling of gases between air, water, and soil is especially important for the pollutants of concern that are characterized by chemists as "semi-volatile" in nature. These semi-volatile pollutants coexist in the atmosphere in both the gas and particle phases, and can revolatilize into the air after deposition (though not as readily as volatile compounds such as benzene or vinyl chloride). Semi-volatile organic compounds include PAHs, PCBs, and several pesticides (e.g., hexachlorobenzene, α-HCH, and lindane), as well as the metallic form of mercury and many of the other 188 toxic pollutants listed as hazardous air pollutant (HAPs) in section 112(b) of the CAA. Because these compounds possess very low vapor pressures and water solubilities, they are distributed between the gaseous and particulate phase both in the atmosphere and in the water column, and their distribution among air, water, soil, and vegetation is very complex. This makes tracking or modeling movements of semi-volatile compounds very difficult. Each pollutant has particular chemical-physical attributes affecting phase distribution, so quantitative assessment requires that each pollutant be well understood. Some of the pollutants of concern can be chemically persistent, maintaining chemical identity (not being broken down) as they move among physical phases and, in many cases, into biological tissues. Some other pollutants (such as PAHs) may change to compounds that are bioaccumulative and more toxic than the parent compounds. Other groups of compounds may separate into individual components due to interactions and relative movement among solids and liquids in the environment (Wania and Mackay 1993).

Once released to the environment, persistent semi-volatile compounds may repeatedly cycle between the atmosphere, land, and waterbodies. This cycle can extend over long time periods, resulting in transport of the compounds for long distances. Long-distance transport with repeated deposition to land or water and then revolatilization to the atmosphere has been shown to occur in response to seasonal temperature changes, among other factors (Wania and Mackay 1996). Other factors that influence the extent and duration of this cycling include volatility and persistence of the substance; molecular weight; concentrations and temperatures in air, soil, and water; and atmospheric circulation, pressure, and weather conditions. As the seasons change, the behaviors of atmospheric contaminants change relative to their location in physical media; therefore, sampling work and modeling calculations must be adjusted, for each compound, to correctly estimate their presence and impacts. Warmer conditions on seasonal and global scales generally favor net movement into the atmosphere. Often redeposition takes place in areas of colder atmospheric temperatures (Wallace et al. 1996; Wania and Mackay 1993, 1996). The modeling of chemical fate and concentrations of semi-volatile pollutants over very

large areas is challenging, and lack of data on pollutant source and release makes the validation of existing models difficult (Wania and Mackay 1996). Also, the lack of definitive methods to measure the concentration of the mix of gases, particles, and liquid droplets that constitutes some of the organic semi-volatile pollutants being deposited poses significant challenges for validation of models.

III.B Atmospheric Transport and Deposition Models

The emission, transport, transformation, and deposition of pollutants to the Great Waters is a complex series of processes involving different pollutants that have different behaviors in air and water systems, over very large geographic areas. Therefore, numerous models, as well as input parameters for these models, have been and continue to be developed or evaluated for estimating the atmospheric transport and deposition processes for the various pollutants associated with the Great Waters.

Atmospheric transport and deposition models are used to:

- Predict the direction and distances pollutants will travel in the environment;

- Test hypotheses about characterizations of atmospheric transformations and removal;

- Assist in designing monitoring networks for efficiency and specific analyses, and in placing a limited number of monitors effectively;

- Provide calculated estimates to fill spatial and temporal gaps in monitoring networks, to provide a smooth or coherent picture for analyses;

- Develop relationships between sources and receptors of pollutants; and

- Evaluate prospective pollutant control strategies.

This section discusses different types of models related to atmospheric transport and deposition processes. Results from application of some models presented in this section are described in Chapter IV. The models presented in this section can be classified in three categories: mass balance models, source apportionment techniques, and air quality simulation models.

Mass balance models analyze all ways that pollutants can enter and exit a waterbody, and their corresponding amounts over a period of time (commonly referred to as the pollutant loading). In other words, mass balance models consider the mass (or weight) of a pollutant that is exchanged across interfaces between air, water, land, and sediments as inputs and outputs, to assess the relative loadings of a pollutant into a waterbody by different pathways.

Source apportionment techniques attempt to link sources and receptors of pollutants of interest. Primary source apportionment techniques include *dispersion models, receptor models, and hybrid models*. Dispersion models trace pollutants from their sources to the air at given locations

(e.g., a waterbody). Receptor models trace pollutants in the air at a given location back to particular source types. Hybrid models are similar to receptor models, but also incorporate meteorological data, and work from both the source end and the receptor end of the pollutant transport analysis. One important uncertainty related to source apportionment techniques is the lack of complete and reliable input data, such as the composition and emissions of some pollutant sources. In addition, source apportionment techniques cannot be applied well for air pollutants that are widespread in the environment, travel over long distances, and/or are emitted in large quantities from natural sources or broad area sources. A review of source apportionment techniques for organic compounds, with special emphasis on the Great Waters, is presented by Keeler et al. (1993).

> **Mass Balance Models.** Estimate inputs and outputs of a pollutant to a waterbody (i.e., total amounts of a given pollutant that enter and exit a water body by each of the various pathways).
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> **Source Apportionment Techniques.** Estimate the relative contribution of different sources to air pollutant levels at a specific receptor site (e.g., a particular air mass over Lake Michigan on a particular day).
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> **Air Quality Simulation Models.** Use extensive source emission inventories, meteorological data, and algorithms to simulate processes such as dispersion of pollutants in the atmosphere, transformation of compounds, and deposition.

Air Quality Simulation Models (AQSMs) are used to characterize both the transport and deposition of pollutants. As input data, these models use extensive source emission inventories and meteorological data. AQSMs include algorithms to simulate processes such as dispersion of pollutants in the atmosphere, transformation of compounds, and deposition. The models' results typically include air concentrations and deposition rates of pollutants over a given area for a specified period of time. Although comprehensive, AQSMs are limited by the quality of input data, the computational difficulties of their algorithms, and the modeling of some processes (e.g., air-surface exchange).

The remainder of this section presents additional information on specific applications of the model types mentioned above, especially those that have been recently applied to Great Waters studies. The following subsections focus on mass balance models, receptor models, and AQSMs.

Mass Balance Models

A mass balance model provides the essential framework for determining the relative contribution of pollutant loadings from various mechanisms of input (e.g., direct discharge, river input, atmospheric deposition) and output (e.g., sedimentation, volatilization, outflow) to and from a waterbody. Mass balance models are also helpful to relate concentration measurements to pollutant mass fluxes between different media (air, waterbodies, land surface) and to mass of a contaminant in different environmental "pools" (e.g., a waterbody, a land region). As introduced in the First Report to Congress, when reliable information is available for contributions from the various sources, mass balance models may be used to estimate the importance of atmospheric deposition (or any other mechanism) in causing contamination of a waterbody. Mass balance models usually are good at recognizing sizable pollutant sources and receptors, but often lack the resolution needed to deal with multiple smaller sources that by themselves are not significant, but added together could be important in some situations.

Mass balance studies have provided insights on atmospheric deposition issues relevant to the Great Waters. A review of studies on relative atmospheric loadings of toxic contaminants and nitrogen to the Great Waters is presented by Baker et al. (1993). These studies have provided quantitative estimates indicating that: (1) atmospheric deposition can be the main contributor of toxic chemical contamination and nitrogen enrichment to the Great Waters, although uncertainties still exist; (2) the importance of atmospheric load for a specific pollutant in a given waterbody depends on characteristics of the waterbody, chemical properties, and source locations; and (3) chemicals may cycle between soil, air, water, and biota for many years.

The First Report to Congress presented mass balance case studies for some Great Waters pollutants of concern, such as PCBs in Lake Superior, mercury in lakes in Wisconsin, and nitrogen in the coastal waters of several Atlantic states. Considerable research continues on the development and use of mass balance models for the pollutants of concern in the Great Waters. The Lake Michigan Mass Balance Study, an EPA-sponsored research project, is responsible for a comprehensive sampling effort in Lake Michigan, including measurements of pollutants such as PCBs, trans-nonachlor (a component of technical grade chlordane), mercury, and atrazine in the atmosphere, tributaries, open lake water, sediments, and food chain (fish tissue). Samples collected over a two-year period (1994-1995) for modeling will be used to improve understanding of key environmental processes that govern cycling and bioavailability of contaminants within the Lake Michigan ecosystem. The approach modifies the classic mass balance within a closed system to consider inputs from transport, including long-range transport. Analysis of some selected modeling runs is expected in 1998. A more detailed discussion of this mass balance project is described in Section IV.A.

Receptor Models

Receptor models, which are one type of source apportionment technique, trace pollutants in the air at various locations (such as over a waterbody) back to particular source types in order to estimate the contribution to pollutant levels from a group of sources with similar emissions. This type of model does not use the detailed meteorological data or extensive emission inventories used in air quality simulation models. Receptor models assume that chemicals of concern are affected in the same way by all of the processes involved in pollutant transport and dispersion. This is a particularly useful assumption, but it presents some difficulties when clouds are present, when precipitation occurs, or when extensive chemical transformations of a pollutant are known to occur. A limitation of the receptor models is the lack of adequate "source profile" data, which allow air pollution to be linked to a particular source type. Source profiles refer to "signatures" or "fingerprints" of emissions from a

> **Receptor Model for Great Waters**
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> A project on atmospheric deposition in the Great Waters, entitled Atmospheric Exchange Over Lakes and Oceans (AEOLOS), was started in 1993 by EPA and scientists from the Universities of Minnesota, Michigan, Maryland, Delaware, and the Illinois Institute of Technology. The objectives of this 4-year research program are to determine: (1) the dry depositional fluxes of critical urban contaminants to northern Chesapeake Bay off Baltimore and southern Lake Michigan off Chicago; (2) the contributions of urban source categories to measured atmospheric concentrations and deposition; and (3) the air-water exchange of contaminants and their partitioning into aquatic phases. The contaminants being studied include mercury, trace metals, PAHs, and PCBs. Techniques involve using all three modeling approaches described below -- CMB, PCA, and trajectory analyses. Research is expected to be published in 1998.

type or category of sources; these profiles are determined through samples taken from the actual emissions (i.e., from the "smokestacks") followed by analyses comparing the chemical signature to those of other categories of sources. Despite the limitations of receptor models, these models provide useful insights into contaminant transport to the Great Waters (see sidebar on the previous page).

Some receptor model types include:

♦   *Chemical mass balance (CMB)*: The CMB model assumes that emission characteristics (i.e., chemical and elemental composition, physical size, morphology) of various source types are sufficiently different from one another that their contributions to a receptor may be identified by measuring the characteristics in samples collected at the site. The observed concentration pattern of an ambient sample at the receptor site is equated to a linear combination of the appropriate pollutant source patterns, each weighted by an unknown source strength term. The primary application of the CMB model has been to urban areas such as Chicago and Baltimore. CMB models assume composition of all contributing sources are known, and when this is not the case the uses of the model are limited.

♦   *Principal component analysis (PCA)*: The objective of PCA is to use mathematical analyses to find a minimum number of factors, or source categories, that explain most of the variance in a set of measurements from a receptor site, instead of using all sources as in the CMB models. The number of statistically significant factors is usually found to be six or less. PCA is often limited because it lacks fine resolution of contribution from various distant sources. An advantage of PCA is that ancillary measurements (e.g., wind speed, wind direction, relative humidity) may be incorporated into the analysis along with pollutant concentrations.

♦   *Trajectory clustering*: In these models, a back trajectory is computed using wind data, and the spatial probability of an air "parcel" reaching a particular receptor site at a particular time is calculated. Under different meteorological conditions, all potential trajectories and concurrent pollutant measurements are grouped into a more manageable set of source clusters and regions. A variant of this approach is being used to assess mercury deposition in the Great Lakes basin (see sidebar).

> **Trajectory Clustering Technique
> in the Great Lakes**
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> To determine the sources of mercury deposition to the Great Lakes Basin, a regional network of 10 monitoring sites was established in 1993 by EPA and the University of Michigan to measure atmospheric mercury over several years. The sampling will continue into 1997. Data will be analyzed, using an improved trajectory clustering technique, to determine the sources and source areas most responsible for mercury deposition to the Great Lakes.
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> Source: Burke and Keeler 1995.

Air Quality Simulation Models

Air quality simulation models (AQSMs) are used to characterize the emission, transport, and deposition of hazardous air pollutants over large geographic areas. These models incorporate fairly extensive source emission inventories and meteorological data bases (e.g., wind fields, temperature, mixing height), and apply the collected data to simulated processes

such as dispersion, transformation, and deposition. The models are run to generate estimates of pollutant concentrations and deposition rates over a spatial and temporal pattern. AQSMs are based on two approaches. In one approach, characteristics or properties of air are assigned to fixed points in space at a given time. The second approach is based on a two- or three-dimensional grid system for the geographical pattern of interest, and all the fundamental processes (e.g., emissions, chemical and physical transformations, deposition) of discrete air parcels are considered to occur within the individual grids or boxes.

The mathematical relationships between emissions and concentration (or deposition) are typically nonlinear, due to the influences of atmospheric transport, chemical and physical transformation, and deposition processes. AQSMs attempt to model the nonlinear physical and chemical processes influencing atmospheric concentrations and deposition. AQSMs may be useful tools in providing the analytical framework required to predict the environmental impacts of proposed emission control programs and, consequently, performing both scientific and regulatory assessments.

This section describes two of the various AQSMs that have been developed and peer-reviewed in recent years, the Regional Lagrangian Model of Air Pollution (RELMAP) and the Regional Acid Deposition Model (RADM). These two models (among others presented in Section III.C) have been used in Great Waters studies, and their results are presented in Chapter IV. Another model being developed for application to atmospheric deposition in the Great Waters is discussed in the sidebar.

RELMAP is used to simulate the emission, transport, and diffusion of pollutants, their chemical transformations, and wet and dry deposition. The model was originally designed for sulfur analysis (the User's Guide is presented in Eder et al. (1986)). It has also been applied to mercury and other toxic metals (Bullock et al. 1997; Clark et al. 1992), among others. For example, the goal of one study was to determine the extent of mercury emissions to air in the United States over an entire year, the deposition to U.S. soil and waterbodies, and the contribution by source category to the total amount of mercury emitted and deposited within the United States (Bullock et al. 1997). Section III.C presents relevant applications and limitations of this model.

RADM has been developed over the last ten years under the National Acid Precipitation Assessment Program (NAPAP) to address policy and technical issues associated with acidic deposition (Chang et al. 1990; Dennis et al. 1990). The version of RADM used for NAPAP models an area east of Central Texas and south of James Bay, Canada, to the southern tip of Florida. This

> **A Model for Assessing Atmospheric Deposition to the Great Waters**
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> EPA has recently developed a new modeling tool for the assessment of atmospheric deposition of pollutants to the Great Waters. The Regulatory Modeling System for Aerosols and Deposition (REMSAD) is a work station-based Eulerian model intended for use in assessing the impacts of regulatory activities, such as the MACT standards, on loadings of pollutants of concern to the Great Waters. REMSAD is currently capable of simulating short-, medium-, and long-range transport and deposition of cadmium, dioxins, mercury, and POM. Nitrate deposition distributions have been produced through REMSAD simulation, but have not yet been compared to other models such as RADM. Other pollutants, including other toxics, be incorporated in future work. Initial model demonstration and evaluation will be completed during 1997. The model is currently available on the OAQPS Support Center for Regulatory Air Models (SCRAM) bulletin board.

area is divided in a grid, and for each grid cell the model considers pollutant emissions, transport in and out of the cell, turbulent motion in the atmosphere, chemical reactions that produce or deplete the chemical, vertical transport by clouds, and removal by dry deposition. RADM is designed to model 140 chemical reactions among 60 pollutants, 40 of which are organic compounds. A feature of RADM is the simultaneous modeling of sulfur and nitrogen deposition. This is an important consideration because the amount of sulfur dioxide (SO_2) present in the atmosphere affects the formation of both sulfates and nitrates and thus, the amount and spatial distribution of nitrogen deposited back to waterbodies. RADM is also useful for analyzing long-range transport issues, but it is very complex computationally. Recently, it has been applied to the study of nitrogen deposition in the Chesapeake Bay watershed (Dennis 1997).[9] The results of this study are presented in Section IV.C. The limitations of this study, as well as more background information on RADM, are presented in Dennis (1997).

AQSMs are limited by the quality of the algorithms used to simulate various processes affecting pollutants of interest (e.g., chemical transformation, deposition), quality of input data (e.g., emissions, meteorology), and lack or inadequacy of modeling of certain processes (e.g., air/water gas exchange). The quantity and quality of available input data is an important limiting factor in the application of AQSMs, especially for atmospheric pollutants, such as many pesticides and PCBs, that have relatively poorly developed emission inventories, or for which re-emission and environmental cycling are significant.

Efforts sponsored by the Great Waters program are underway to improve the quality of emission estimates for the HAPs, which historically have been inventoried only in a few places and for short time intervals. In one effort, the eight states that border the Great Lakes have worked together, with EPA, to develop an approved protocol for a coordinated emission inventory of 49 HAPs, including the Great Waters pollutants of concern other than pesticides. The inventories for point sources and area sources, as well as mobile sources, should be completed by 1997-1998. The data are stored in a regional data base system (the Regional Air Pollutant Inventory Development System, or RAPIDS) developed for this project. In another effort, EPA is in the process of developing national inventories of sources and emissions for seven specific HAPs (hexachlorobenzene, alkylated lead compounds, PCBs, POM, mercury, 2,3,7,8-TCDD, and 2,3,7,8-TCDF) in response to the mandate in section 112(c)(6) of the CAA.

III.C Comparing Models Used in Great Waters Studies

Several numerical atmospheric transport and deposition models or modeling strategies have been and continue to be developed and used for understanding deposition of pollutants to the Great Waters. Models have many roles in EPA's atmospheric programs and are widely used to link emissions data, meteorology, receptor sites (e.g., people, or lakes, exposed to pollutants), and monitoring of the ambient air (in cities, or over lakes for the Great Waters). New approaches to modeling have been needed to deal with the particular complexities of the issues in Great Waters studies. To discuss these models and their applications to the Great Waters with the general scientific community, the EPA Great Waters program co-sponsored a session at the 15th

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[9] Work by Dennis (1997) models nitrate deposition only; however, ammonium and organic nitrogen deposition may also be quantitatively important to the Bay.

annual meeting of the Society of Environmental Toxicology and Chemistry (SETAC) in 1994 on "Atmospheric Deposition of Nutrients & Contaminants." Following that meeting, the presenters and other scientists prepared written chapters for a SETAC Special Publication: *Atmospheric Deposition of Contaminants to The Great Lakes and Coastal Waters*, J.E. Baker, editor (Baker 1997). This section briefly describes the main applications and limitations of the models presented in the SETAC session. This presentation is not intended to be a comprehensive list of all existing models and their uses, as the development of transport and deposition models is a very active research area. The document based on the SETAC session (Baker 1997) provides an in-depth technical reference that supplements the information in this report.

Table III-1 summarizes some of the relevant modeling efforts. These models are further discussed below, with a very brief description of the model, its application to Great Waters studies, and how the model compares with actual monitoring data; further information is presented in Baker (1997).

The first modeling effort listed in Table III-1 is the regional-scale analysis of nitrogen deposition to the Chesapeake Bay watershed (Dennis 1997). The analysis was developed using RADM, described in Section III.B. The overall goals of this study are, first, to define the source region that contributes most of the nitrogen deposition affecting the Chesapeake Bay watershed and, second, to define which source types are most responsible. The modeling results indicate that the range of influence of nitrogen emissions is on the order of 800 kilometers (km) (though this is considered a conservative estimate, given the model bias described in the study). The model indicates that the source region for nitrogen deposition in the Chesapeake Bay watershed is roughly 906,000 km^2, or more than 5.5 times larger than the watershed. Dennis (1997) also uses the model to analyze the spatial distribution of nitrogen deposition by emission sector. For example, the model results indicate that utility emissions tend to be more responsible for nitrogen deposition to the Bay basins themselves, while mobile emissions appear to influence deposition to the mouths of the tributaries and the Bay itself. Additional results of this modeling effort are presented in Section IV.C, although the study does not present any comparison to monitoring data. The study does highlight the importance of additional research on the bias in RADM for nitrogen deposition estimates, processes such as forest or terrestrial retention of nitrogen, and the combined use of air-water models.

The second modeling analysis in Table III-1 looks at wet and dry deposition of semi-volatile organic compounds at a regional scale, with emphasis on the Great Lakes (Ching et al. 1997). The model used is a version of the Regional Particulate Model (RPM), which is itself a modification of RADM that computes the chemical composition and size distribution of the secondary sulfur and nitrogen species (Binkowski and Shankar 1993). Ching et al. (1997) use RPM to analyze the size, chemical composition, and moisture content of airborne particles that serve as sites for condensation and volatilization of semi-volatile organic compounds. Deposition of semi-volatile organic compounds is tracked in the model as proportional to particle deposition. This modeling effort is a step toward the use of regional-scale models to compute air concentrations of these pollutants, and to provide benchmark testing of simpler and computationally less demanding models. Some challenges ahead in this line of modeling include better algorithms and data on air-water gas exchange, the role of clouds as both transporters and chemical transformers, and modeling of resuspension of pollutants from different land uses.

As presented in Table III-1, the numerical modeling of atmospheric mercury by Bullock et al. (1997) uses the model RELMAP (Eder et al. 1986), described in Section III.B, with relatively simple mercury parameterizations. An entire year of transport and deposition of airborne mercury was simulated over the continental United States. The goals of this modeling effort were to analyze the amount of mercury emitted to the air annually over the United States that is deposited back to U.S. soils and waterbodies, the contribution of mercury by source category, and the importance of long-range transport. The RELMAP-simulated annual results agree with the majority of the limited annual deposition and concentration data available around the Great Lakes and in Florida, as well as other areas, usually within a factor of two. Some RELMAP estimates of wet deposition of mercury are somewhat high when compared to actual measurements at those locations. However, the model cannot be well tested over the entire model domain without annual observations in a large number of additional locations. The limitations of this current research effort, including modeling of certain meteorological conditions, aqueous chemistry of mercury, and transport and diffusion modeling are presented in Bullock et al. (1997).

Pirrone and Keeler (1997) propose a hybrid receptor-deposition modeling approach to estimate the dry deposition flux and air-water gas exchange of various HAPs to Lake Michigan. The approach combines modeling of over-water transport of air masses and modeling of deposition and gas exchange. The model parameters were calibrated using data from the Lake Michigan Urban Air Toxics Study (LMUATS) to find both the temporal and spatial variation of critical parameters controlling the transport and deposition of atmospheric contaminants. The results of this study indicate large variations in the parameter values and hence the uncertainty associated with the common practice of using constant parameter values for modeling. The work by Pirrone and Keeler (1997) demonstrates a different approach to estimating surface flux quantities that currently cannot be directly measured with confidence.

TABLE III-1
Summary of Atmospheric Transport and Deposition Models Applied to the Great Waters[a]

Model	Description of Model	Great Waters Related Application	Goodness of Fit[b]	References
Regional Acid Deposition Model (RADM)	Developed under the NAPAP to predict regional changes that may occur as a result of nitrogen and sulfur deposition. The geographic area covered by the model is the eastern U.S. and Canada.	Project quantity and spatial distribution of deposition to the Chesapeake Bay watershed from sources in eastern U.S. and Canada. Estimate fraction that each of 15 subregions in the area contribute to total annual load of atmospherically deposited nitrogen to the Bay watershed and tidal waters.	Comparisons within a factor of 2 for sulfur deposition, and generally within a factor of 2 for nitrogen deposition.	Dennis (1997)
Regional Particulate Model (RPM)	Based on RADM; computes the chemical composition and size distribution of the secondary sulfur and nitrogen species, to identify airborne particles that may serve as sites for condensation or volatilization.	Predict wet and dry deposition of airborne semi-volatile organic toxic compounds to the Great Lakes on a regional scale.	Theoretical only and has not been compared with actual data.	Ching et al. (1997)
Regional Lagrangian Model of Air Pollution (RELMAP)	Simulates concentrations of wet and dry deposition patterns of gaseous pollutants and particulate matter (both fine and coarse), and can generate source-receptor matrices for user-defined regions.	Model deposition of metals including cadmium and lead to Lake Superior; model the emission, transport, and fate of airborne mercury in the U.S., including the Great Lakes and Florida.	Wet deposition results from RELMAP for atmospheric mercury agree with the majority of actual measurements within a factor of 2.	Bullock et al. (1997)
Hybrid receptor-deposition model	Uses backward trajectory calculations and estimates dry deposition and gas exchange flux. Parameters incorporated into the model include transport distance, meteorological conditions, particle size distribution, and water surface roughness.	Estimate deposition of trace metals and semi-volatile organic compounds to Lake Michigan for the Lake Michigan Urban Air Toxics Study.	Experimental model; variation in the model depended on the nature of the chemical species and was ± 3-fold that of values in literature.	Pirrone and Keeler (1997)

[a] Models were presented at 1994 SETAC Annual Meeting and are described in Baker (1997).
[b] "Goodness of fit" refers to how well the deposition estimates from the models correspond to actual measured deposition data.